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WHICH ELECTRONIC AND STRUCTURAL FACTORS CONTROL THE PHOTOSTABILITY OF DNA AND RNA PURINE NUCLEOBASES?

MARVIN POLLUM, CHRISTIAN REICHARDT, CARLOS E. CRESPO-HERNÁNDEZ, *Chemistry, Case Western Reserve, Cleveland, OH, USA*; LARA MARTÍNEZ-FERNÁNDEZ, INÉS CORRAL, *Departamento de Quimica, Universidad Autonoma de Madrid, Madrid, Spain*; CLEMENS RAUER, SEBASTIAN MAI, PHILIPP MARQUETAND, LETICIA GONZÁLEZ, *Institute for Theoretical Chemistry, University of Vienna, Vienna, Austria*.

Following ultraviolet excitation, the canonical purine nucleobases, guanine and adenine, are able to efficiently dissipate the absorbed energy within hundreds of femtoseconds. This property affords these nucleobases with great photostability. Conversely, non-canonical purine nucleobases exhibit high fluorescence quantum yields or efficiently populate long-lived triplet excited states from which chemistry can occur. Using femtosecond broadband transient absorption spectroscopy in combination with ab initio static and surface hopping dynamics simulations we have determined the electronic and structural factors that regulate the excited state dynamics of the purine nucleobase derivatives. Importantly, we have uncovered that the photostability of the guanine and adenine nucleobases is not due to the structure of the purine core itself and that the substituent at the C6 position of the purine nucleobase plays a more important role than that at the C2 position in the ultrafast relaxation of deleterious electronic energy. [The authors acknowledge the CAREER program of the National Science Foundation (Grant No. CHE-1255084) for financial support.]